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REPORT ON

NON-NEWTONIAN FLUID MECHANICS

(Molecular Mechanisms)

March 2, 1966

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<u>Contractor</u>:   UNIVERSITY OF PENNSYLVANIA

<u>Address</u>: The School of Chemical Engineering
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<u>Objective</u>:   The purpose of this research is to determine and study the molecular mechanisms responsible for Newtonian and non-Newtonian viscosity in high-polymer melts and solutions.

BACKGROUND

Discussions of the need for studies of the molecular origins of non-Newtonian behavior of polymer fluids and of our approach to this problem were given in the proposal in solicitation of NsG 667.[1] These discussions will not be repeated in detail, but we feel it would be useful to summarize the scientific and technological background that motivates our approach to the problem.

We consider two rheological experiments characterizing polymer melts and solutions. In the first case we subject the fluid to a constant rate of (simple) shear and define an apparent non-Newtonian viscosity η by the relationship

$$\tau = \eta \dot{\gamma}$$

where τ is the shear stress and $\dot{\gamma}$ is the shear rate. In the second case we subject the fluid to a small sinusoidal shear γ^*;

$$\gamma^* = \gamma_0 \exp(i\omega t)$$

where γ_0 is the amplitude of the oscillation, ω is the angular frequency and t is time. We then observe a sinusoidally varying shear stress τ^*;

$$\tau^* = \tau_0 \exp(i\omega t + i\delta)$$

where τ_0 is the amplitude of the varying shear stress and δ is the angle by which stress and strain are out of phase. If the material is a non-viscoelastic fluid δ is $90°$. From this second experiment, called the dynamic experiment, we can also define a viscosity, the dynamic viscosity η^*;

$$\tau^* = \eta^* \dot{\gamma}^* = \eta^* \, i\omega\gamma^*$$

where $\dot{\gamma}^*$ is the time derivative of γ^*. The dynamic viscosity η^* is a complex number and is written

$$\eta^* = \eta' - i\eta''$$

where η' is the real part and η'' the imaginary part., Just as η is a function of $\dot{\gamma}$, we find that η^* is a function of ω.

It is reasonable to ask just what the relationship between these two viscosities might be since they measure energy dissipation of the macromolecular systems under greatly different circumstances. Apparent viscosity is obtained from a large-strain experiment in which the polymer chains are grossly removed from their equilibrium positions, and at high shear rates the chains can be greatly deformed. Dynamic viscosity, however, is obtained from a small-strain experiment in which the polymer chains undergo small oscillatory perturbations about their equilibrium positions. One relationship between the two viscosities can be derived from phenomenological linear viscoelasticity theory with no dependence upon any molecular model.[2] It can be shown that

$$\lim_{\dot{\gamma} \to 0} \eta = \lim_{\eta \to 0} \eta^* = \lim_{\omega \to 0} \eta'$$
$$(\text{since } \lim_{\omega \to 0} \eta'' = 0)$$

These expressions can also be derived from irreversible statistical machines starting from the usual random flight model for polymer molecules.[3,4] The above equations simply tell us that at sufficiently small values of $\dot{\gamma}$ and ω the values of η and η' should be equal. Experimentally we find the values η and η' begin to decrease with increasing $\dot{\gamma}$ and ω at about the same critical value for the shear rate and angular frequency. In the past, it has often been concluded from experiment that, at least semiquantitatively, [5,6,7]

$$\eta(\overset{\bullet}{\gamma}) = \eta'(\omega) \quad \text{when } \overset{\bullet}{\gamma} = \omega$$

or sometimes that (8,9)

$$\eta(\overset{\bullet}{\gamma}) = \left[\eta'(\omega)^2 + \eta''(\omega)^2\right]^{1/2}$$

when $\overset{\bullet}{\gamma} = \omega$. These observations have been given some support [10,11] from theories which base non-Newtonian behavior on chain distortion during flow.

It now seems clear, however, that previously observed equivalence of η and η^* was an experimental coincidence applicable only to a very limited range of values of $\overset{\bullet}{\gamma}$ and ω. More recent work covering extended ranges of frequency and shear rate for polyethylene melt demonstrates deviation of the to viscosity functions.

Even though $\eta^*(\omega)$ and $\eta(\overset{\bullet}{\gamma})$ are not the same functions of their respective arguments, it should not be assumed that the two viscosities are not related. Both can be interpreted as manifestations of molecular relaxation. Problems in molecular mechanics of polymer chains can be treated by normal coordinate analysis. [3,4] To each normal mode of motion we can relate a friction factor (or drag coefficient) which, in turn, defines a corresponding relaxation time. The study of dynamic viscosity over a broad range of frequencies gives a detailed picture of the normal modes of motion and the corresponding relaxation times of polymer chains. [3,4] We should be able to interpret non-Newtonian viscosity in terms of the response of these same normal modes to a constant shear gradient. If it is assumed, as has most after been the case, [3,4] that the same relaxation times (or drag coefficients) apply to both the dynamic and steady shear experiments the most rigorous of theories predict

polymer solutions and melts to be Newtonian fluids.[3,4] This
disappointing result has had some tendency to discredit the
"molecular relaxation" interpretation of polymer viscosity.
Arguments have been presented, however, that relaxation times
should not be the same in the two cases. For example, Groessley[13]
postulates that long chain molecules become less entangled during
steady flow and thus demonstrate shorter relaxation times. He
gives a kinetic model for entanglement-disentanglement equilibrium
that is shifted toward disentanglement by a constant shear
gradient. The essence of his model is not unlike that arrived
at by Brodkey from quite different considerations.[14] Con-
sidering the simplicity of the entanglement - disentanglement
model, agreement between theory and experiment is good. The
fact still remains, however, that there are few dynamic and
steady flow viscosity data on well characterized polymer systems
with chich to test theory.

A rather straightforward experiment can be designed which
would demonstrate whether or not chain entanglements play a pre-
dominate role in non-Newtonian behavior of polymer melts and
solutions. From dynamic viscosity we can determine directly
the extent of molecular entanglement. By measuring dynamic
response superimposed upon steady flow we can determine the
extent of molecular entanglement as a function of shear rate.[13]
If chain entanglement is responsible for non-Newtonian behavior
we should observe (from our superimposed dynamic measurements)
a decreasing entanglement density with increasing shear rate.
If we should observe entanglement density independent of shear
rate we would have to abandon the concept of non-Newtonian vis-
cosity being due to decreasing entanglement density. We would
then be forced to consider again chain distortion models or look
for some new approach to understanding non-Newtonian flow based

on molecular mechanism. To this author's knowledge the experiment
described above has never been done. As we will point out later
in the report, we plan to modify our present equipment to en-
able us to make dynamic measurements superimposed upon steady
non-Newtonian flow.

PROGRESS AND RESULTS

THEORETICAL

In the proposal submitted for this grant,[1] we described a set of normal coordinates in which the equations of motion for an assembly of linear polymer molecules could be separated. These normal coordinates turn out to be the same as those obtained by transforming to the appropriate set in which we can write the square of the radius of gyration as the sums of squares of the coordinates. This principal investigator has studied this normal coordinate system in depth.[15,16,17] This separation of variables reduces the development of theories of dynamic and steady flow viscosities to problems in non-equilibrium statistical mechanics. Several dynamic viscosity theories were developed that were in good agreement with experiment.[3,4] Application of the same techniques to steady flow viscosity yielded results predicting polymer melts and solutions to be Newtonian fluids. Early in the period of this grant we also attacked the problem of predicting η from molecular structure. Although we feel gratified that we obtained a solution to the problem by going further back to first principle than our predecessors, we were hardly elated by the fact that we got the exact same wrong answer - namely that polymer melts and solutions are Newtonian fluids. Nevertheless, because of the close relationship between our theoretical approach to viscosity and the theory of polymer dimensions, we believe this work is sufficiently illuminating to warrant publication. The results of this work will be submitted to the Journal of Chemical Physics with a title such as "Relationships Between Configurational Statistics and Flow Mechanism of Linear Polymer Molecules".

As an aside, we should like to point out that the early theoretical works on dynamic and steady flow viscosity[3,4] preceeded this author's work on the configurational statistics of linear polymer molecules[15,16,17] and the equivalence of the normal coordinate systems was never appreciated.

Our theoretical approach to steady flow viscosity, as the others, assumed molecular entanglement to be independent of shear rate. It has been shown,[13] however, that removal of this assumption yields a theory in qualitative agreement with experiment. The relationship between entanglement density and shear rate was quite arbitrary, and whether or not this modification of the molecular relaxation theory has real physical significance will have to be determined by experiments other than steady flow viscosity (we will suggest doing just such experiments later in this report.)

So far all theoretical treatments of dynamic and steady flow viscosity have been restricted to linear molecules. We have begun extending our normal coordinate analysis to branched polymer molecules. When this work is completed we should be able to apply it directly to predicting dynamic viscosity of branched polymer. If entanglement density is indeed a function of shear rate, we should be able to apply the same type "entanglement correction" to predict steady flow viscosity of branched polymer. Our work (to date) on the configurational statistics of branched polymer molecules was presented at the "First Middle Atlantic Regional Meeting" of the American Chemical Society in Philadelphia, Penna., on February 4, 1966. An abstract of the talk is included at the end of this report. When the manuscript is completed copies will be sent to NASA for the NsG 66 file.

EXPERIMENTAL

1. Viscosity

Although this report covers the 18 months of the existence of NsG 667, our research group was formed in January, 1965 and has been active for only about one year. Much of this time has been spent in setting up, equipping, and organizing two new polymer research laboratories. We have received support from three sources to study the broad area of molecular relaxation and flow in polymer melts and solutions. The largest support is from NsG 667 with somewhat less from the University of Pennsylvania (administering ARPA funds) and an N.S.F. research initiation grant. During these early stages of the research we find it difficult to assign the specific origin of support for any particular piece of work since our activity has been largely restricted to: (1) selection, construction, and testing steady state and dynamic viscometers, (2) bringing the graduate students up to a sufficient level of experimental and/or theoretical sophistication that they can do relatively independent work, (3) rather general computer programming associated with flow and molecular relaxation (4) developing auxiliary experimental techniques such as preparation of monodisperse polymer, preparation of uniform polymer solutions (of high viscosity) and recovery of polymer from solution. Consequently we will describe our total progress and activity in the field of relaxation and flow in high-polymer systems.

A Haake Rotovisco viscometer was obtained for our steady
state viscosity measurements on polymer solutions. It is
equipped with cup-and-bob and cone-and-plate attachments. Our
tests show the instrument capable of measuring viscosity as a
function of shear rate on our polystyrene solutions from 15%
to 50% polymer. This covers the concentration range of most
interest to us at present, but we plan to get a second cup-and-
bob attachment to enable us to go to much lower concentrations.

The instrument to measure dynamic viscosity is now com-
pleted, however, we plan a continuing program of modification
and improvement of the equipment. The "heart" of the dynamic
viscometer is the Haake Rotovisco. The Rotovisco is driven
in a sinusoidal mode with a multi-frequency torsional pendulum.
The resonance frequency of the pendulum is designed to be varied
between 0.05 and 1000 cycles per sec. by varying the torsion
bar and inertial elements. The amplitude of the pendulum is
measured with an optical-electronic transducer system. At
frequencies of a few cycles/sec. or lower, the output of the
phototube is recorded. At 10 cycles/sec. and higher, the out-
put of the phototube is rectified and the envelope recorded.
Motion of the pendulum is also monitored with an oscilliscope.
The period of the vibration is measured with a Hewlett-Packard
counter. By measuring resonance frequency and log-decrement
of the pendulum-viscometer system with and without sample, we
can determine the dynamic viscosity of the polymer melts or
solutions.

The torsion pendulum operates well between 0.1 and 100 cycles per sec., but mechanical instability makes measurements impossible at higher frequencies. We have redesigned the system incorporating a nearly frictionless air bearing. If our calculations are correct, lateral motion of the inertial element will be held to $\pm 3 \times 10^{-4}$ inch. After many modifications we have developed an optical-electronic system that operates adequately. We expect to improve our signal to noise ratios, however, by further electrical and light shielding.

A schematic of the dynamic visometer was shown in a recent NsG 667 report.[18] Instrument constants for the dynamic viscometer have been obtained by calibration with non-viscoelastic (and Newtonian) mineral oil. We have made our "shakedown" runs comparing dynamic and steady flow viscosities of 10% and 50% polystyrene solutions in decalin. The polymer was commerical material with weight average molecular weight of about 200,000. The results of this initial work were presented at the "First Middle Atlantic Regional Meeting" of the American Chemical Society in Philadelphia, Penna., on February 4, 1966. The data presented is shown at the end of this report. Figure 1 shows the results of measurements on the dilute solution. As was expected, the solution was nearly Newtonian and non-viscoelastic. In this case we would expect η' and η to be equal. Agreement is excellent. Figure 2 shows the results of measurements on the concentrated solution. We note that below about 50 sec.$^{-1}$ this solution is also newtonian and η' should equal η. Agreement is again excellent. Above about 50 sec.$^{-1}$ the concentrated solution shows non-Newtonian behavior and, as would he expected, η' falls off with increasing

angular frequency. Unfortunately, just as we were beginning
our high frequency measurements the servomotor of the recorder
burned out. Because of the trouble with the servomotor, data
for the highest frequency point (Fig. 2) was erratic and we could ex-
pect that point to be considerably in error (possibly ± 20%).
Nevertheless, we feel that the instrument works as we had
planned and with some modification and minor improvements it
will be suitable for carrying out the research as originally
proposed.

2. AUXILIARY RESEARCH

We have recently completed our first successful anionic
polymerization aimed at making monodisperse polystyrene. As
of yet, we have not evaluated our product. We hope our synthetic
work is successful since to be able to prepare our own polymer
samples will give our program far greater flexibility. The
lack of availability of monodisperse polymer is not as serious
as it was last year, however, since it is now available com-
mercially at about ten dollars per twelve grams.

Since much of work will be with solutions of viscosities
in excess of 100 Poise, forming homogeneous solutions becomes
a major problem. We have designed a special mixer which we
feel will do the job. As far as we can tell to date it works
well.

In anticipation of obtaining our first steady state and
dynamic viscosities, we have written a computer program to
calculate viscosities and a number of viscoelastic functions
(creep compliance, stress relaxation, dynamic modulus, dynamic

compliance and loss factor). The program as it now exists will calculate all of the above functions from the Rouse-Bueche relaxation theory, but it can be easily modified to do the calculations starting from any discrete distribution of relaxation times.

We have completed setting up equipment for the characterization of polymer. We now have operational facilities for measuring weight average molecular weight and polymer chain dimensions by light scattering and number average molecular weight by osmometry. Equipment for routine intrinsic viscosity measurement is also now operational.

FUTURE PLANS

We have developed the capability of measuring study flow and dynamic viscosities of polymer solutions as described in the proposal for NsG 66. We can now turn our attention to studying these viscosities as a function of molecular structure. We will start our experimentation by looking at monodisperse polystyrene. We will then extend our work to include more complex system: (1) branched monodisperse polymer (2) polymer of controlled molecular weight distribution, (3) block and random copolymers.

Concurrent with interpretation of our experimental data we plan to spend time considering viscosity theory. Just what we will do in this area is hard to define until more experimental results are available with which to examine existing theory. What we definitely plan, however, is continued studies of normal coordinate analysis of branched polymer chains extending current viscosity theory to included branched polymer molecules.

We plan a significant addition to our experimental program. We have devised a technique of superimposing dynamic measurements upon steady flow by modification of our existing dynamic viscometer. This can be accomplished by rotating the cup (or plate) at a constant rate while monitoring damped oscillation of the bob (or cone). By this technique we hope to establish experimentally the relationship between non-Newtonian flow and chain entanglement.

The work described above is directed toward studying dynamic and steady state viscosities of polymer solutions. During the coming year (1966) we plan to extend our research to include polymer melts – a more difficult area of experimentation. For our study of steady state viscosities, the University has purchased an Instron Rheometer (a high pressure capillary viscometer) costing about five-thousand dollars. For our study of the dynamic visocity of polymer melts, we plan to use the Haak instrument driven (as for polymer solutions) by the torsional pendulum. We have found, however, that before we can use this system with melts we will have to redesign and rebuild the cone-and-plate attachments. Rebuilding is necessary to obtain adequate temperature control at the temperatures required for the study of polymers with glass transitions greater than about 50°C.

Conclusions

We propose to extend our current research in molecular mechanisms of non-Newtonian flow of polymers to include:

1. Measurement of dynamic viscosity superimposed upon steady flow as a tool for studying shear rate dependence of molecular entanglement.

2. Further developing our equipment to enable us to measure both dynamic and steady flow viscosity or polymer melts.

In addition we plan to continue our current activity in studying non-Newtonian flow of concentrated polymer solutions.

Appendix

/7. Abstract of paper presented by W. C. Forsman
at the "First Middle Atlantic Regional Meeting"
of the American Chemical Society in Philadelphia,
Pa. on February 4, 1966.

/8. Dynamic and steady flow viscosities of 10%
solutions of polystyrene in decolin at about
30°C. Molecular weight of the polymer was
about 200,000.

/9. Dynamic and steady flow viscosities of 50%
solutions of polystyrene in decolin at about
30°C. Molecular weight of the polymer was
about 200,000.

ON THE CONFIGURATION OF BRANCHED POLYMER MOLECULES.
William C. Forsman. (University of Pennsylvania).

Application of statistical mechanics to predict the behavior of branched polymer molecules has, in general, been reasonably success-ful. (1,2) The present formulation, however, is not entirely satisfac-tory in the approach to such problems as linear viscoelastic behavior. We chose therefore, to approach the problem of treating branched mole-cules from a different point of view with hopes of developing a some-what more general formulation. In this paper, we present the results of applying this type of analysis to calculation of the root-mean-square radius of gyration of unperturbed chains with various types of branching.

In a previous paper we showed that the x component of the radius of gyration, S_x, can be written $(tS_x)^2 = [\gamma]^T[a][\gamma]$ where $[\gamma]$ is the column matrix of the x components of the vectors connecting adjacent masses in the flexible chain, t is the number of statistical elements in the chain, and $[a]$ is a txt symmetric matrix with elements $a_{ij}=(t+1-i)j$ if $i \geqslant j$ and $a_{ij}=(t+1-j)i$ if $j \geqslant i$. We further showed that $t^2 \langle s^2 \rangle = \langle \gamma^2 \rangle$ trace$[a]$.

In this paper we show that for branched molecules we can write $(tS_x)^2 = [\gamma]'[D][\gamma]$ where $[D]=[C]^T[a][C]$ and $[C]$ and, $[D]$ are determined only by the nature of the branching. It follows, then, that for branched molecules

$$t^2 \langle s^2 \rangle = \langle \gamma^2 \rangle \text{ trace } [D] .$$

We applied the above technique of analysis to the general cruciform molecule with branches of k, l, m, and n segments. We express the results in terms of g which is the ratio of $\langle S^2 \rangle$ for a given branched chain to $\langle S^2 \rangle$ for a linear chain of the same number of statistical segments. If we write $\kappa =(k/t)$, $\lambda = (1/t)$, $\mu = (m/t)$, and $\gamma = (n/t)$ we find that

$$g = 1-6[\kappa\lambda\mu + \kappa\lambda\gamma + \kappa\mu\gamma + \lambda\mu\gamma]$$

We also applied this technique to the uniformly branched, or comb-like, molecule having n branches of b segments on a linear backbone with each branch separated from its nearest neighbors by m backbone segments. The expression for g is again a simple one, and particularly simple if $n \gg 1$. In this latter case, if we write $\mu = nm/t$ (the fraction of segments in the backbone) and $\beta = nb/t$ (the fraction of segments in the branches) we find that $g \cong 1- \beta^3 - \frac{1}{2}\mu\beta^2 - \mu^2\beta$.

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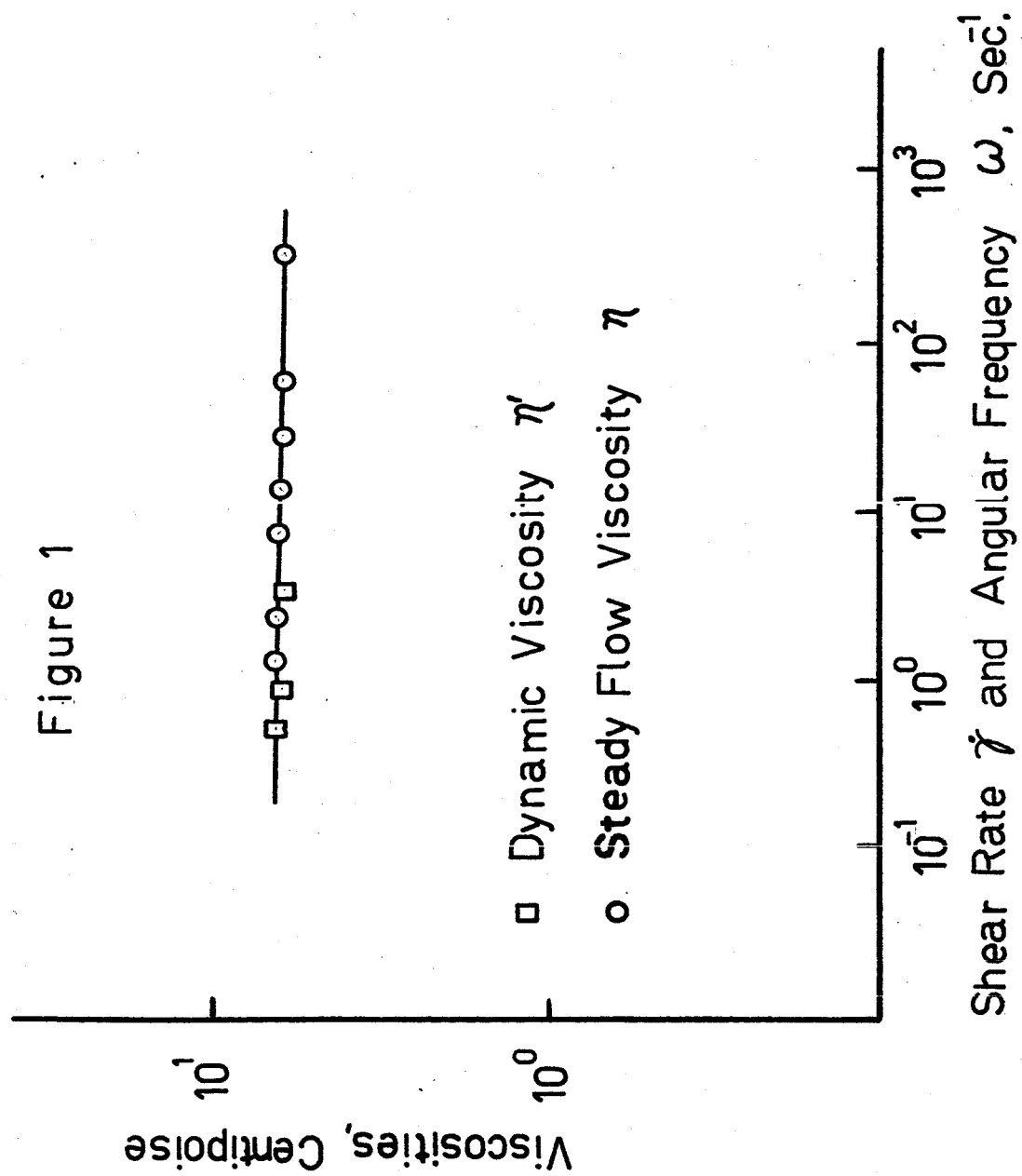
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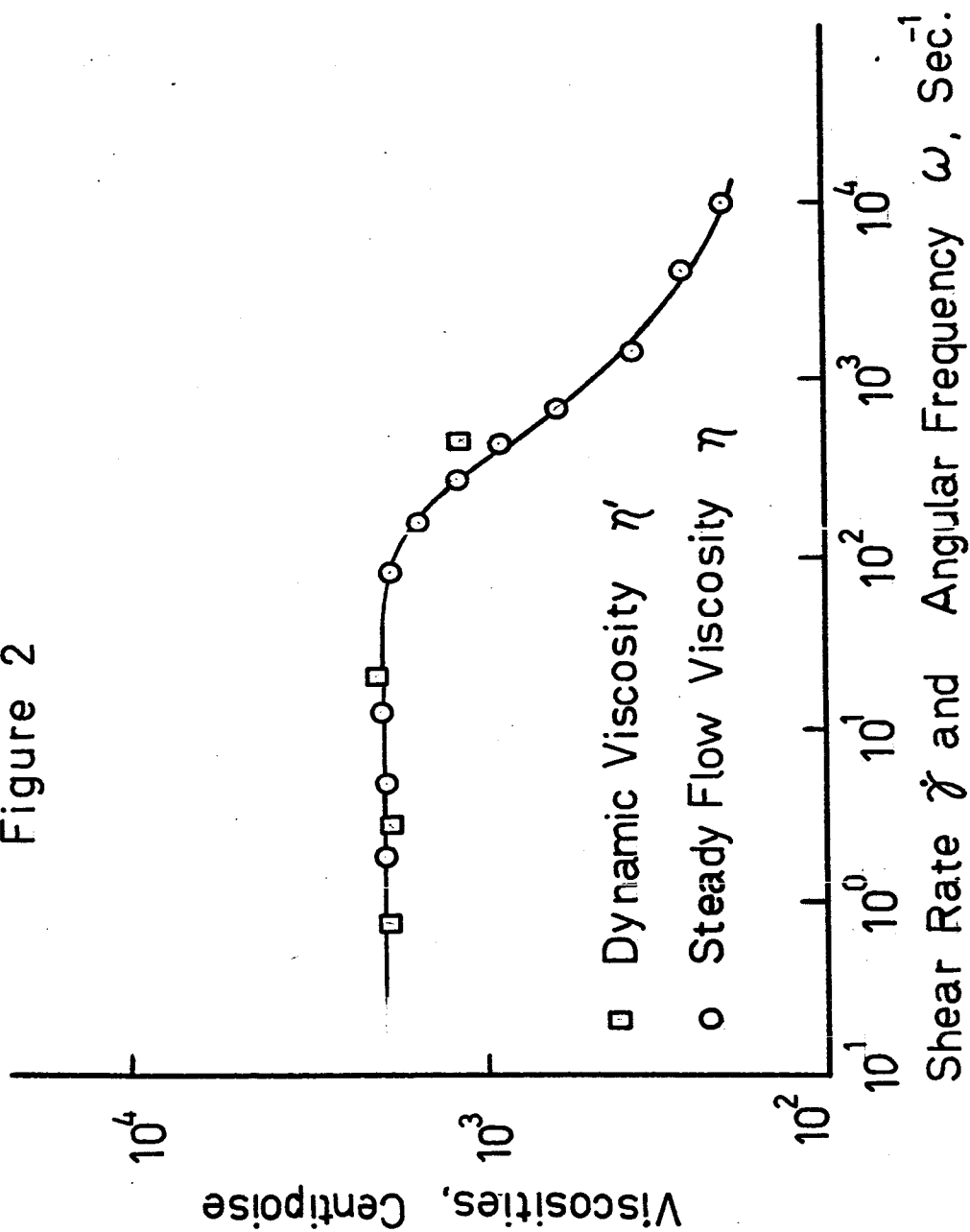
Figure 1

Figure 2

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